

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) PREPARATION OF HOMOGENEOUS PARTLY CRYSTALLINE ETHYLENE COPOLYMERS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the controlled continuous copolymerization of ethylene and one or more  $\alpha$ -olefins to partly crystalline homogeneous random copolymers of closely controlled physical properties, and to the copolymers resulting therefrom.

The copolymerization of ethylene and various  $\alpha$ -olefins (e.g. butene, hexene and octene) using a coordination catalyst system to yield partly crystalline copolymers with a range of physical properties is well known and is described in Canadian Patent 664,211 issued to Anderson and Stamatoff on 4th June, 1963. The partly crystalline copolymers so prepared have a density and a stiffness intermediate between those of a linear polyethylene homopolymer (0.96 g./cc., 140,000 psi) and a completely amorphous ethylene- $\alpha$ -olefin rubber (0.85 g./cc., less than 5000 psi). These partly crystalline copolymers possess physical properties which render them suitable for a wide range of practical applications such as film extrusion, blow moulding, injection moulding, wire coating and paper coating. The copolymer composition and molecular weight are adjusted to the optimum value for the particular end use desired.

In the art, it is well known that within any given copolymer molecule, the comonomer distribution may be random, regular, block or combinations thereof. However, the comonomer distribution between the molecules of the copolymer must also be considered. Upon consideration of the latter distribution factor, two

classes of copolymers have been noted, namely heterogeneous copolymers and homogeneous copolymers.

Heterogeneous copolymers may be defined as those in which the copolymer molecules do not have the same ethylene/comonomer ratio. These copolymers can be differentiated into three basic types dependent upon the degree of heterogeneity and whether the ethylene/comonomer ratio is a function of the size of the molecule. A heterogeneous copolymer (type I) might be defined as one in which the ethylene/comonomer ratio is not a function of the size of the copolymer molecule, i.e. the comonomer content of all the molecular weight fractions is the same but within each such fraction, there are individual molecules with a comonomer content above or below the average. Heterogeneous copolymers might also be defined as those in which the ethylene/comonomer ratio is a function of the molecular weight, with type II copolymers being those in which the ratio increases with molecular weight and type III copolymers being those in which the ratio decreases with molecular weight. Combinations of types I, II and III are also possible.

"Homogeneous copolymers" may be defined as, and the term is used herein to mean those polymers in which not only is the comonomer randomly distributed within a given molecule but all the copolymer molecules have the same ethylene/comonomer ratio. Homogeneous copolymers of narrow molecular weight distribution exhibit a reduced haze level in extruded film, higher impact strength, reduced tendency towards delamination in extruded articles and better balance of physical properties in the machine and transverse direction of extruded film when compared with conventional heterogeneous copolymers.

These subtle but extremely important comonomer distribution features have not been considered in the prior art relating to partly cry-

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stalline ethylene- $\alpha$ -olefin copolymers. It is only with the advent of new instrumental techniques that studies of possible molecular configurations can be made. Previously, fractionation of a whole copolymer into 10 to 20 sharp molecular fractions and subsequent comonomer analysis of the individual fractions had been assumed to offer unequivocal proof of distributional homogeneity of the copolymer. However, a heterogeneous random copolymer (type I) would not show any compositional heterogeneity under these conditions. Therefore, a constant ethylene/comonomer ratio as determined by analysis of sharp molecular weight fractions of a copolymer is a necessary but not a sufficient condition for proof of copolymer homogeneity. An additional and more reliable indication of copolymer homogeneity is the relationship between the crystalline melting point of the whole copolymer (or sharp molecular weight fraction) and its comonomer content.

The ethylene- $\alpha$ -olefin copolymers which are produced following the teachings of the prior art have been found to be random with respect to the comonomer distribution within the copolymer molecule but heterogeneous with respect to the monomer distribution between molecules of the copolymer.

We have now found that by the use of coordination catalysts of narrowly defined composition, ethylene- $\alpha$ -olefin copolymers can be prepared under continuous process conditions which have a narrow molecular weight distribution, a random distribution of comonomer units along the polymer backbone and are homogeneous between molecules with respect to their comonomer content.

According to the present invention, therefore, we provide a continuous process for the preparation of homogeneous random partly crystalline copolymers of narrow molecular weight distribution comprising ethylene and at least one other  $\alpha$ -olefin, at least one such other  $\alpha$ -olefin having four or more carbon atoms, which process comprises polymerizing the monomers dissolved in an inert nonpolymerizable solvent therefor and for the copolymer to be prepared in an agitated reaction zone maintained at a pressure sufficient to maintain the monomers in solution and at a temperature of 40 to 110°C. in the presence of a catalyst prepared by mixing (A) an organo-aluminum halide  $R_nAlX_{3-n}$  wherein R is an alkyl or aryl radical, n is not greater than 1.5 or less than 1.0 and X is Cl or Br and (B) a vanadium compound selected from (1)  $VO(OR)_mX_{3-m}$  where R is an alkyl or aryl radical, m is not less than 1 or more than 3, and X is Cl or Br and (2) vanadium oxyhalides soluble in the reaction medium; provided that when the vanadium compound is of type (1) the vanadium concentration in the reaction zone is not greater than 0.260 millimoles/liter of solution and the Al/V ratio in the reaction zone is not less than 5/1 when the  $\alpha$ -olefin is a  $C_4$  or  $C_5$   $\alpha$ -olefin, not less than 9/1 when the  $\alpha$ -olefin is a  $C_6$  to  $C_{10}$   $\alpha$ -olefin and not less than 12/1 when the  $\alpha$ -olefin is a  $C_{10}$  to  $C_{20}$   $\alpha$ -olefin, and that when the vanadium compound is of type (2) the vanadium concentration in the reactor is not greater than 0.160 millimoles/liter of solution and the Al/V ratio in the reaction zone is not less than 5/1 when the  $\alpha$ -olefin is a  $C_4$  to  $C_6$   $\alpha$ -olefin.

The present invention also comprises a copolymer of ethylene and at least one another  $\alpha$ -olefin, at least one such other  $\alpha$ -olefin having four or more carbon atoms, when made by the process of the invention. Preferably the copolymer has a homogeneity index, as defined hereinafter, in excess of 75, and advantageously in excess of 90 (the definition of homogeneity index does not, however, apply to terpolymers derived from propylene).

The inert solvent used as a reaction medium may be an aliphatic, aromatic or cycloaliphatic hydrocarbon, such as heptane, toluene or cyclohexane. The solvent chosen must be a solvent for the monomer and for the polymer produced in the reaction. Cyclohexane is the preferred reaction medium.

Suitable  $\alpha$ -olefins for use in practicing the process of the present invention are  $\alpha$ -olefins having at least four carbon atoms, such as, for example, 1-butene, 1-hexene, 1-octene, or 1-octadecene. Preferred  $\alpha$ -olefins are 1-butene, 1-octene, a mixture of 1-butene and 1-octene or a mixture of 1-octene and propylene. A preferred catalyst component (A) for these preferred  $\alpha$ -olefins is (ethyl)<sub>1.5</sub> AlCl<sub>1.5</sub> together with either VO(*o*-n-butyl)<sub>2</sub>Cl or VOCl<sub>3</sub> as catalyst component (B). When the vanadium compound, used in preparing the catalyst, is an oxyhalide, the comonomer should not contain more than 9 carbon atoms.

When practicing the process of the present invention, the reaction zone should be maintained substantially free of concentration gradients. This may be accomplished by the use of a well-agitated reactor operating under essentially turbulent mixing conditions.

In the drawings attached hereto:

Figure I is a graph representing the relationship between the copolymer melting point and comonomer content;

Figure II is a graph representing the relationship between copolymer density and comonomer content; and

Figure III is a graph representing the relationship between copolymer melt index and density difference from melt index 1.0.

In Figure I, lines A and B show the relationship between the crystalline melting point and comonomer content for various ethylene- $\alpha$ -olefin copolymers where the  $\alpha$ -olefin is  $\geq C_4$ . Specifically, line A is a plot of equation (1) below which is a computer generated equation based on regression analysis of the melting point — comonomer content data for a series

	of commercially available heterogeneous ethylene-butene copolymers and experimental heterogeneous ethylene-octene copolymers.	<i>Equation (3)</i>
5	<i>Equation (1)</i>	Copolymer Melting Point °C = 130 - 15.77 (CH <sub>3</sub> /100C + vinyl/100C) + 0.818 (CH <sub>3</sub> /100C + vinyl/100C) <sup>2</sup> embodiment of the present invention.
10	<i>Copolymer Melting Point °C =</i> 130 - 7.42 (CH <sub>3</sub> /100C + vinyl/100C) + 0.414 (CH <sub>3</sub> /100C + vinyl/100C) <sup>2</sup> Since heterogeneity is a relative rather than absolute term, it is obvious that no single melting point vs. comonomer content relationship can be defined for all heterogeneous copolymers.	In Figure II, line A shows the relationship between copolymer density and comonomer content for heterogeneous copolymers of ethylene with $\alpha$ -olefins having at least four carbon atoms and line B shows this relationship for homogeneous copolymers of ethylene with $\alpha$ -olefins having at least four carbon atoms.
15	Line B of Figure I is a plot of equation (2), a computer generated relationship based on regression analysis of the melting point-comonomer content data for copolymers prepared under the preferred conditions of the present invention (runs 11—28, Table II).	Figure II shows that in the case of homogeneous copolymers the amounts of comonomer required for a given copolymer density is considerably less than that required for a heterogeneous copolymer of equivalent density. This density difference is a useful index of copolymer homogeneity.
20	<i>Equation (2)</i>	The following examples will help to illustrate the present invention:
25	<i>Copolymer Melting Point °C =</i> 130 - 18.51 (CH <sub>3</sub> /100C + vinyl/100C) + 0.967 (CH <sub>3</sub> /100C + vinyl/100C) <sup>2</sup> It is evident, from Figure I, that copolymers which are not homogeneous in comonomer content show crystalline melting points at a given comonomer content which are significantly higher than the melting points of homogeneous copolymers of the same comonomer content. Homogeneous - random ethylene- $\alpha$ -olefin copolymers (where the $\alpha$ -olefin is $\geq C_4$ ) are defined therefore as those copolymers whose crystalline melting point is related to their comonomer content by equation 2. Copolymers with melting points greater than that predicted by equation 2 are heterogeneous to the extent that their melting point exceeds the value given of equation 2. If this melting point is elevated by comonomer heterogeneity to the point where it exceeds the value predicted by equation 3 below, the copolymer is considered sufficiently heterogeneous to fall outside the specific	Several runs were made using a well agitated continuous reactor system operating under essentially turbulent mixing conditions such that a constant environment, substantially free of concentration gradients, was maintained in the reactor. Ethylene, the desired $\alpha$ -olefin or $\alpha$ -olefins, the catalyst components and hydrogen if desired for melt index control were dissolved in the inert solvent and fed into the reactor, which was maintained under varying pressures, for varying contact times. The process conditions and the results of these runs were tabulated in Tables I—VIII which follow.
30	Copolymers with melting points greater than that predicted by equation 2 are heterogeneous to the extent that their melting point exceeds the value given of equation 2. If this melting point is elevated by comonomer heterogeneity to the point where it exceeds the value predicted by equation 3 below, the copolymer is considered sufficiently heterogeneous to fall outside the specific	Polymer properties referred to hereinafter in the Tables were determined by the following methods.
35	40	<i>Melt Index</i> ASTM D-1238
45	Equation 3 defines the melting point of copolymers whose homogeneity index, as defined hereafter, is equal to 75.	<i>Stress Exponent</i> The stress exponent is determined by measuring the throughput in a melt indexer at two stresses (2160 g. and 6480 g. loading) using procedures similar to the ASTM melt index procedure
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$$S.E. = \frac{1}{0.477} \left( \log_{10} \frac{\text{wt. extruded with 6480 g. wt.}}{\text{wt. extruded with 2160 g. wt.}} \right)$$

#### Melting Point

The differential thermal analysis determination of melting point was made using a Perkin-Elmer differential scanning calorimeter (DSC) calibrated for temperature with indium metal and flushed with dry nitrogen gas at a flow rate of 40 mls/min.

The samples were in the form of discs 1/4" in diameter, 3 to 4 mils thick and about 2 mg. in weight. Prior to the melting point deter-

mination, the samples were heated to 180°C. in the DSC apparatus, held there for 5 minutes and then cooled at a rate of 10°C./min. to 30°C. The melting points were determined on the subsequent melting profiles obtained at a heating rate of 20°C./min. The melting point was taken as the peak of the highest melting endotherm. Homogeneous copolymers were characterized by a sharp melting endotherm. Increased copolymer heterogeneity

tended to broaden the melting endotherm as well as to raise the temperature at which the endotherm occurred.

Since the melting point data on polymer systems are critically dependent on annealing conditions, it is essential that the samples be put through the same melting-cooling cycle prior to melting point determination.

#### Comonomer Analysis

The determination of total alkyl groups was made by the ASTM method "Tentative Method of Test for Alkyl Groups in Polyethylenes based on Infrared Spectrophotometry — Proposed Revision of D2238—64T" using method A-11 — Standard Sample Compensation Method.  $K'_{1878}$  for alkyl groups greater than  $C_3$  was taken to be 0.110;  $K'_{1878}$  for ethyl groups was taken to be 0.074 and the factor  $f_{1878}$ , obtained by calibration with octane, was determined to be 141.5. The total number of alkyl groups was determined and reported in terms of total methyl groups per 100 carbon atoms.

The number of side chain methyl groups was obtained by subtracting the number of terminal methyl groups from the total number of methyl groups. The number of terminal methyl groups was calculated from the following formula:

$$30 \quad \text{No. of terminal methyl groups} = V + 2Vd + 2T$$

where  $V$  = number of vinyl groups/100 carbon atoms

$$35 \quad Vd = \text{numbers of vinylidene groups}/100 \text{ carbon atoms}$$

$$T = \text{number of trans groups}/100 \text{ carbon atoms}$$

The concentration of vinyl, vinylidene and trans unsaturation groups in the copolymers was determined by infrared spectrophotometric absorbances at 908, 889 and 965  $\text{cm}^{-1}$  using molar extinction coefficients of 121.0, 103.4 and 85.4 respectively.

For normal alkyl groups the number of side chain methyl groups also represents the number of branches and is related directly to the comonomer content of the copolymers.

#### Copolymer Density

Copolymer density was determined by ASTM Method D1505—63T. Since copolymer density is related to both comonomer content and copolymer molecular weight (or melt index), the observed density was corrected to melt index 1.0 using the relationship given in Figure III.

#### Homogeneity Index

We use this term herein to mean an empirical value of copolymer homogeneity obtained from Figure I by taking the melting point difference between lines A and B, at any given  $\text{CH}_3/100\text{C}$  content, as equal to 100. The homogeneity index of a copolymer is, therefore, taken as its relative position between these two guide lines.

Mathematically the homogeneity index of a given copolymer can be calculated from its melting point and comonomer content using equation (4) below.

#### Equation (4)

$$\text{HI} = 100 \left( \frac{130 - 7.42 (\text{CH}_3) + 0.414 (\text{CH}_3)^2 - \text{MP}_{rc}}{11.09\text{CH}_3 + 0.553 (\text{CH}_3)^2} \right)$$

70 where

$\text{HI}$  = homogeneity index

$\text{CH}_3$  = total  $\text{CH}_3/100\text{C}$  + vinyl/100C

$\text{MP}_{rc}$  = melting point of copolymer

It should be noted that only homogeneous copolymers of ethylene and  $\alpha$ -olefins of at

least four carbon atoms follow the melting point relationship of equation 2 or line B of Figure I. The determination of homogeneity index is not applicable, therefore, to terpolymers where propylene is one of the comonomers.

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TABLE I  
Copolymerization Synthesis Conditions — Heterogeneous Copolymers

Run No.	1	2	3	4
Ethylene Feed (g./min.)	19.6	16.2	16.1	0.257
Comonomer	1-Butene	1-Octene	1-Butene	1-Butene
Comonomer Feed (g./min.)	11.8	13.1	4.4	0.105
Solvent (ml./min.)	361	364	400	14.64
Cocatalyst	(Isoprenyl) <sub>3</sub> Al	(Isoprenyl) <sub>3</sub> Al	(Isoprenyl) <sub>3</sub> Al	(Isobutyl) <sub>2</sub> AlCl
Catalyst	VOCl <sub>3</sub> —TiCl <sub>4</sub> V/Ti = 3.0	VOCl <sub>3</sub> —TiCl <sub>4</sub> V/Ti = 3.0	VOCl <sub>3</sub>	V(acetylacetone) <sub>3</sub>
Cocatalyst/catalyst ratio	1.48	1.50	5	10.8
Catalyst conc. in reactor millimoles/liter)	0.22	0.49	0.51	0.197
Reactor Temp., °C.	195	176	126	100
Reactor contact time (min.)	2.06	2.05	6.3	2.7
Ethylene conversion	0.924	0.978	0.846	0.770
Copolymer Melt Index (M.I.)	2.85	1.50	2.21	22.0

TABLE I (Continued)  
Copolymerization Synthesis Conditions — Heterogeneous Copolymers

Run No.	5	6	7	8
Copolymer Stress Exponent	1.38	1.37	1.61	—
Copolymer Density	0.9220	0.9217	0.9206	0.9287
Copolymer Density (corr. to M.I. 1.0)	0.9197	0.9207	0.9187	0.9227
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	2.00	2.10	1.84	1.49
Copolymer side chain CH <sub>3</sub> /100C	1.80	2.01	1.70	1.43
Copolymer melting point, °C.	116.7	119.7	116.5	115.0
Homogeneity Index	0	-17	-10	18
Hydrogen (micromoles/min.)	nil	nil	2430	26.5
Catalyst formation conditions	Premixed	Premixed	In situ	In situ

TABLE I (Continued)  
Copolymerization Synthesis Conditions — Heterogeneous Copolymers

Run No.	5	6	7	8
Ethylene Feed (g./min.)	0.257	0.257	0.257	0.257
Comonomer	1-Butene	1-Butene	1-Octene	1-Octene
Comonomer Feed (g./min.)	0.105	0.163	0.257	0.257
Solvent (ml./min.)	14.72	14.75	13.36	12.62
Cocatalyst	(Isobutyl) <sub>2</sub> AlCl	(Isobutyl) <sub>2</sub> AlCl	(Ethy) <sub>2</sub> AlCl	(Ethy) <sub>2</sub> AlCl <sub>2</sub>
Catalyst	V(acetylacetone) <sub>3</sub>	VOCl <sub>3</sub>	VO(O-n-buryl) <sub>3</sub>	VOCl <sub>3</sub>
Cocatalyst/catalyst ratio	5.7	14.4	14.9	15.4
Catalyst Conc. in reactor millimoles/liter)	0.197	0.092	0.126	0.54
Reactor Temp., °C.	100	100	100	120
Reactor contact time (min.)	2.7	2.68	2.97	3.14
Ethylene conversion	0.822	0.547	0.619	0.538
Copolymer Melt Index (M.I.)	1.37	8.1	11.2	1.20

TABLE I—Continued  
Copolymerization Synthesis Conditions — Heterogeneous Copolymers

Run No.	1	2	3	4
Copolymer Stress Exponent	1.36	1.34	—	2.07
Copolymer Density	0.9225	0.9253	0.9368	0.9347
Copolymer Density (corr. to M.I. 1.0)	0.9207	0.9210	0.9318	0.9342
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.65	1.32	1.28	1.15
Copolymer side chain CH <sub>3</sub> /100C	1.59	1.20	1.19	0.98
Copolymer melting point, °C.	113.4	115.4	113.9	118.8
Homogeneity Index	20	51	18	36
Hydrogen (micromoles/min.)	12.4	23.1	20.3	nil
Catalyst formation conditions	In situ	In situ	In situ	In situ

TABLE I (Continued)  
Copolymerization Synthesis Conditions — Heterogeneous Copolymers

Run No.		9	10
Ethylene Feed (g./min.)		0.260	0.256
Comonomer	1-Butene		1-Octene
Comonomer Feed (g./min.)	0.118		0.257
Solvent (ml./min.)	12.90		12.23
Cocatalyst	(Ethy)AlCl <sub>2</sub>		(Ethy)AlCl <sub>2</sub>
Catalyst	VOCl <sub>3</sub>		VOCl <sub>3</sub>
Cocatalyst/catalyst ratio	15.0		15.0
Catalyst conc. in reactor millimoles/liter)	0.48		0.58
Reactor Temp., °C.	122		122
Reactor contact time (min.)	2.97		3.25
Ethylene conversion	0.479		0.536
Copolymer Melt Index (M.I.)	12.3		0.87

TABLE I (Continued)  
Copolymerization Synthesis Conditions — Heterogeneous Copolymers

Run No.	9	10
Copolymer Stress Exponent	—	—
Copolymer Density	0.9366	0.9311
Copolymer Density (corr. to M.I. 1.0)	0.9314	0.9315
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.00	1.46
Copolymer side chain CH <sub>3</sub> /100C	0.86	1.31
Copolymer melting point, °C.	116.1	108.9, 116.5, 119.6
Homogeneity Index	65	5
Hydrogen (micromoles/min.)	nil	nil
Catalyst formation conditions	In situ	In situ

TABLE II  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	11	12	13	14
Ethylene Feed (g./min.)	0.257	0.257	0.257	0.257
Comonomer	1-Octene	1-Octene	1-Octene	1-Octene
Comonomer Feed (g./min.)	0.257	0.257	0.257	0.257
Solvent (ml./min.)	12.22	12.23	12.29	12.22
Cocatalyst	(Ethyl)AlCl <sub>2</sub>	(Ethyl) <sub>1.25</sub> AlCl <sub>1.75</sub> *	(Ethyl) <sub>1.6</sub> AlCl <sub>1.5</sub> **	(Ethyl)AlCl <sub>2</sub>
Catalyst	VO(O-n-butyl) <sub>3</sub>	VO(O-n-butyl) <sub>3</sub>	VO(O-n-butyl) <sub>3</sub>	VOCl <sub>3</sub>
Cocatalyst/catalyst ratio	14.8	14.9	14.7	15.3
Catalyst conc. in reactor millimoles/liter)	0.203	0.134	0.138	0.132
Reactor Temp., °C.	100	100	100	100
Reactor contact time (min.)	3.25	3.25	3.23	3.25
Ethylene conversion	0.620	0.557	0.583	0.445
Copolymer Melt Index (M.I.)	11.5	1.41	2.13	5.21

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	15	16	17	18
Copolymer Stress Exponent	—	1.30	1.17	1.19
Copolymer Density	0.9217	0.9243	0.9219	0.9259
Copolymer Density (corr. to M.I. 1.0)	0.9618	0.9236	0.9203	0.9223
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.27	0.94	1.08	1.02
Copolymer side chain CH <sub>3</sub> /100C	1.13	0.84	0.99	0.91
Copolymer melting point, °C.	108.8	111.6	110.8	112.6
Homogeneity Index	93	116	103	95
Hydrogen (micromoles/min.)	nil	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ	In situ

\* 3 mole (ethyl)AlCl<sub>2</sub>, 1 mole (ethyl)<sub>2</sub> AlCl

\*\* 1 mole (ethyl)<sub>2</sub>AlCl 1 mole (ethyl)AlCl.

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	15	16	17	18
Ethylene Feed (g./min.)	0.257	0.257	0.138	0.258
Comonomer	1-Butene	1-Butene	1-Butene	1-Octene
Comonomer Feed (g./min.)	0.0970	0.202	0.0913	01.50
Solvent (ml./min.)	12.78	13.23	6.56	12.75
Cocatalyst	(Ethyl)AlCl <sub>2</sub>	(Ethyl) AlCl <sub>2</sub>	(Ethyl) AlCl <sub>2</sub>	(Ethyl) AlCl <sub>2</sub>
Catalyst	VO(O-n-buty)₃	VO(O-n-buty)₃	VO(O-n-buty)₃	VO(O-n-buty)₃
Cocatalyst/catalyst ratio	15.3	14.7	15.1	14.8
Catalyst conc. in reactor millimoles/liter)	0.129	0.123	0.122	0.0973
Reactor Temp., °C.	100	100	100	100
Reactor contact time (min.)	3.10	3.00	6.05	3.11
Ethylene conversion	0.686	0.546	0.564	0.577

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	19	20	21	22
Copolymer Melt Index (M.I.)	3.3	9.16	2.08	0.58
Copolymer Stress Exponent	1.19	1.09	1.22	1.24
Copolymer Density	0.9235	0.9193	0.9154	0.9241
Copolymer Density (corr. to M.I. 1.0)		0.9148		0.9262
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.10	1.56	1.39	0.67
Copolymer side chain CH <sub>3</sub> /100C	1.04	1.48	1.32	0.60
Copolymer melting point, °C.	110.7	105.6	107.1	115.8
Homogeneity Index	100	86	93	130
Hydrogen (micromoles/min.)	nil	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ	In situ

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	19	20	21	22
Ethylene Feed (g./min.)	0.257	0.257	0.257	0.256
Comonomer	1-Octadecene	1-Octene	1-Octene	1-Octene
Comonomer Feed (g./min.)	0.579	0.257	0.0858	0.130
Solvent (ml./min.)	12.99	12.89	13.43	14.06
Cocatalyst	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>
Catalyst	VO(O-n-buty)₃	VO(O-n-buty)₃	VO(O-n-buty)₃	VO(O-n-buty)₃
Cocatalyst/catalyst ratio	14.7	11.2	14.0	14.4
Catalyst conc. in reactor millimoles/liter)	0.129	0.131	0.123	0.117
Reactor Temp., °C.	100	100	100	100
Reactor contact time (min.)	3.06	3.08	2.95	2.82
Ethylene conversion	0.532	0.557	0.677	0.602

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	23	24	25	26
Copolymer Melt Index (M.I.)	6.94	5.29	1.11	1.47
Copolymer Stress Exponent	1.18	1.22	1.25	1.24
Copolymer Density	0.9210	0.9220	0.9282	0.9263
Copolymer Density (corr. to M.I. 1.0)	0.9168	0.9183		
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.26	1.22	0.54	0.74
Copolymer side chain CH <sub>3</sub> /100C	1.10	1.12	0.46	0.67
Copolymer melting point, °C.	107.3	110.2	116.9	115.1
Homogeneity Index	100	89	160	122
Hydrogen (micromoles/min.)	nil	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ	In situ

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	23	24	25	26
Ethylene Feed (g./min.)	0.257	0.257	0.363	0.257
Comonomer	1-Octene	1-Octene	1-Octene	1-Octene
Comonomer Feed (g./min.)	0.257	0.257	0.363	0.770
Solvent (ml./min.)	12.17	12.18	18.10	15.09
Cocatalyst	(Ethy) <sub>1.5</sub> AlCl <sub>1.5</sub>			
Catalyst	VO(O-n-butyl) <sub>3</sub>	VO(O-n-decy) <sub>2</sub> Cl	VO(O-n-decy) <sub>2</sub> Cl	VO(O-n-decy) <sub>2</sub> Cl
Cocatalyst/catalyst ratio	13.35	14.0	10.0	10.0
Catalyst conc. in reactor millimoles/liter)	0.136	0.133	0.140	0.177
Reactor Temp., °C.	100	100	90	50
Reactor contact time (min.)	3.27	3.25	3.77	4.79
Ethylene conversion	0.557	0.547	0.610	0.762

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	23	24	25	26
Copolymer Melt Index (M.I.)	2.97	3.12	1.35	2.63
Copolymer Stress Exponent	1.18	1.20	1.22	1.15
Copolymer Density	0.9227	0.9210	0.9142	0.8770
Copolymer Density (corr. to M.I. 1.0)	0.9201	0.9183	0.9134	0.8746
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.06	1.16	1.68	4.80
Copolymer side chain CH <sub>3</sub> /100C	1.00	1.08	1.60	4.70
Copolymer melting point, °C.	110.8	110.0	104.3	63.0
Homogeneity Index	104	98	84	99
Hydrogen (micromoles/min.)	nil	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ	In situ

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	27	28
Ethylene Feed (g./min.)	0.258	5.0
Comonomer	1-Butene	1-Butene
Comonomer Feed (g./min.)	0.287	2.9
Solvent (mL./min.)	15.08	220
Cocatalyst	(Ethy) <sub>1.6</sub> AlCl <sub>1.5</sub>	(Ethy)AlCl <sub>2</sub>
Catalyst	VO(O-n-decy) <sub>2</sub> Cl	VOCl <sub>3</sub>
Cocatalyst/catalyst ratio	9.9	15.0
Catalyst conc. in reactor millimoles/liter)	0.0917	0.205
Reactor Temp., °C.	50	100
Reactor contact time (min.)	4.92	8.8
Ethylene conversion	0.810	0.650

TABLE II (Continued)  
Copolymer Synthesis Conditions — Homogeneous Copolymers

Run No.	27	28
Copolymer Melt Index (M.I.)	0.89	20.2
Copolymer Stress Exponent	1.11	1.19
Copolymer Density	0.8950	0.9184
Copolymer Density (corr. to M.I. 1.0)	0.8980	0.9125
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	3.56	1.50
Copolymer side chain CH <sub>3</sub> /100C	3.54	1.40
Copolymer melting point, °C.	76.3	103.9
Homogeneity Index	99	102
Hydrogen (micromoles/min.)	17.7	nil
Catalyst formation conditions	In situ	In situ

TABLE III  
Effect of Comonomer Size on Copolymer Homogeneity

Run No.	29	30	31	32
Ethylene Feed (g./min.)	0.257	0.257	0.257	0.257
Comonomer	1-Octene	1-Octadecene	1-Butene	1-Octene
Comonomer Feed (g./min.)	0.257	0.579	0.0808	0.257
Solvent (ml./min.)	12.22	13.02	12.88	12.62
Cocatalyst	(Ethyl)AlCl <sub>2</sub>	(Ethyl)AlCl <sub>2</sub>	(Ethyl)AlCl <sub>2</sub>	(Ethyl)AlCl <sub>2</sub>
Catalyst	VOCl <sub>3</sub>	VOCl <sub>3</sub>	VOCl <sub>3</sub>	VOCl <sub>3</sub>
Cocatalyst/catalyst ratio	15.3	14.8	14.1	15.0
Catalyst conc. in reactor millimoles/liter)	0.132	0.130	0.538	0.528
Reactor Temp., °C.	100	100	100	105
Reactor contact time (min.)	3.25	3.05	3.09	3.16
Ethylene conversion	0.445	0.420	0.722	0.605

TABLE III (Continued)  
Effect of Comonomer Size on Copolymer Homogeneity

Run No.	29	30	31	32
Copolymer Melt Index (M.I.)	5.21	2.96	17.4	1.28
Copolymer Stress Exponent	1.19	1.39	—	2.05
Copolymer Density	0.9259	0.9230	0.9250	0.9287
Copolymer Density (corr. to M.I. 1.0)	0.9223	0.9204	0.9195	0.9280
Copolymer total CH <sub>3</sub> /100 C and vinyl unsaturation	1.02	0.93	1.46	1.40
Copolymer side chain CH <sub>3</sub> /100C	0.91	0.80	1.33	1.26
Copolymer melting point, °C.	112.6	108.4, 114.0, 118.8	109.9	107.2, 115.1, 118.8
Homogeneity Index	95	46	66	10
Hydrogen (micromoles/min.)	nil	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ	In situ

TABLE IV  
Effect of Reactor Temperature on Copolymer Homogeneity

Run No.	33	34	35	36
Ethylene Feed (g./min.)	0.257	0.257	0.361	0.360
Comonomer	1-Butene	1-Butene	1-Octene	1-Octene
Comonomer Feed (g./min.)	0.099	0.105	0.361	0.360
Solvent (ml./min.)	12.79	12.76	18.10	17.99
Cocatalyst	(Ethyl)AlCl <sub>2</sub>	(Ethyl)AlCl <sub>2</sub>	(Ethyl) <sub>1.5</sub> AlCl <sub>1.5</sub>	(Ethyl) <sub>1.5</sub> AlCl <sub>1.5</sub>
Catalyst	VO(O-n-buty) <sub>3</sub>	VO(O-n-buty) <sub>3</sub>	VO(O-n-decy) <sub>2</sub> Cl	VO(O-n-decy) <sub>2</sub> Cl
Cocatalyst/catalyst ratio	7.5	7.3	10	10
Catalyst conc. in reactor (millimoles/liter)	0.126	0.122	0.140	0.135
Reactor Temp., °C.	130	150	90	120
Reactor contact time (min.)	2.98	2.90	3.78	3.76
Ethylene conversion	0.440	0.158	0.61	0.36

TABLE IV (Continued)  
Effect of Reactor Temperature on Copolymer Homogeneity

Run No.	33	34	35	36
Copolymer Melt Index (M.I.)	0.0675	2.25	1.35	2.56
Copolymer Stress Exponent	—	2.02	1.22	1.60
Copolymer Density	0.9320	0.9421	0.9142	0.9269
Copolymer Density (corr. to M.I. 1.0)	—	0.9401	0.9134	—
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	0.75	0.75	1.68	1.16
Copolymer side chain CH <sub>3</sub> /100C	0.66	0.58	1.60	1.00
Copolymer melting point, °C.	117.4	120.0	104.3	114.3
Homogeneity Index	91	58	84	62
Hydrogen (micromoles/min.)	nil	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ	In situ

TABLE IV (Continued)  
Effect of Reactor Temperature on Copolymer Homogeneity

Run No.	37	38	39
Ethylene Feed (g./min.)	0.351	0.350	0.351
Cocatalyst	1-Octene	1-Octene	1-Octene
Comonomer Feed (g./min.)	0.361	0.361	0.361
Solvent (ml./min.)	18.06	18.01	17.48
Cocatalyst	(Ethyl) <sub>1.5</sub> AlCl <sub>1.5</sub>	(Ethyl) <sub>1.5</sub> AlCl <sub>1.5</sub>	(Ethyl) <sub>1.5</sub> AlCl <sub>1.5</sub>
Catalyst	VOCl <sub>3</sub>	VOCl <sub>3</sub>	VOCl <sub>3</sub>
Cocatalyst/catalyst ratio	10	10	10
Catalyst conc. in reactor millimoles/liter)	0.136	0.134	0.139
Reactor Temp., °C.	110	115	120
Reactor contact time (min.)	3.69	3.66	3.77
Ethylene conversion	0.30	0.22	0.26

TABLE IV (Continued)  
Effect of Reactor Temperature on Copolymer Homogeneity

Run No.	37	38	39
Copolymer Melt Index (M.I.)	1.56	0.63	0.11
Copolymer Stress Exponent	1.29	1.53	1.85
Copolymer Density	0.9255	0.9290	0.9290
Copolymer Density (corr. to M.I. 1.0)	0.9244	0.9304	—
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	0.97	0.91	1.10
Copolymer side chain CH <sub>3</sub> /100C	0.88	0.81	0.98
Copolymer melting point, °C.	114.3	115.8	116.3
Homogeneity Index	87	80	52
Hydrogen (micromoles/min.)	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ

TABLE V  
Effect of Alky/Aluminum Ratio on Copolymer Homogeneity

Run No.	40	41
Ethylene Feed (g./min.)	0.257	0.257
Comonomer	1-Butene	1-Octene
Comonomer Feed (g./min.)	0.163	0.257
Solvent (ml./min.)	14.75	13.36
Cocatalyst	(Isobutyl) <sub>2</sub> AlCl	(Ethy) <sub>2</sub> AlCl
Catalyst	VOCl <sub>3</sub>	VO(O-n-butyl) <sub>3</sub>
Cocatalyst/catalyst ratio	14.4	14.9
Catalyst conc. in reactor millimoles/liter)	0.092	0.126
Reactor Temp., °C.	100	100
Reactor contact time (min.)	2.68	2.97

TABLE V(Continued)  
Effect of Alkyl/Aluminum Ratio on Copolymer Homogeneity

Run No.	40	41
Ethylene conversion	0.547	0.619
Copolymer Melt Index (M.I.)	8.1	11.2
Copolymer Stress Exponent	1.34	
Copolymer Density	0.9253	0.9368
Copolymer Density (corr. to M.I. 1.0)	0.9210	0.9318
Copolymer total CH <sub>2</sub> 100C and vinyl unsaturation	1.32	1.16
Copolymer side chain CH <sub>3</sub> /100C	1.20	1.10
Copolymer melting point, °C.	113.9	118.8
Homogeneity Index	51	25
Hydrogen (micromoles/min.)	23.1	20.4
Catalyst formation conditions	In situ	In situ

TABLE VI  
Effect of Al/V Ratio on Co/polymer Homogeneity

Run No.	42	43	44	45
Ethyene Feed (g./min.)	0.257	0.257	0.257	0.257
Comonomer	1-Butene	1-Octene	1-Octene	1-Octene
Comonomer Feed (g./min.)	0.099	0.257	0.257	0.257
Solvent (ml./min.)	13.33	13.56	13.03	13.27
Cocatalyst	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>
Catalyst	VO(O-n-butyl) <sub>3</sub>	VO(O-n-butyl) <sub>3</sub>	VO(O-n-butyl) <sub>3</sub>	VO(O-n-butyl) <sub>3</sub>
Cocatalyst/catalyst ratio	5.1	8.8	7.4	4.8
Catalyst conc. in reactor (millimoles/liter)	0.142	0.120	0.126	0.125
Reactor Temp., °C.	100	100	100	100
Reactor contact time (min.)	2.98	2.93	3.04	2.99
Ethyene conversion	0.712	0.602	0.613	0.650

TABLE VI (Continued)  
Effect of Al/V Ratio on Co-polymer Homogeneity

Run No.	42	43	44	45
Copolymer Melt Index (M.I.)	1.47	11.85	4.72	3.78
Copolymer Stress Exponent	1.38	1.13	1.18	1.31
Copolymer Density	0.9210	0.9222	0.9220	0.9234
Copolymer Density (corr. to M.I. 1.0)	0.9200	0.9171	0.9185	0.9204
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.28	1.39	1.34	1.39
Copolymer side chain CH <sub>3</sub> /100C	1.19	1.29	1.22	1.28
Copolymer melting point, °C.	109.8	108.9	106.8, 110.8	106.8, 112.6, 117.3
Homogeneity Index	85	80	71	22
Hydrogen (micromoles/min.)	5.3	21.8	14.1	13.3
Catalyst formation conditions	In situ	In situ	In situ	In situ

TABLE VI (Continued)  
Effect of Al/V Ratio on Copolymer Homogeneity

Run No.		46	47
Ethylene Feed (g./min.)		0.257	0.257
Comonomer	1-Butene		1-Octene
Comonomer Feed (g./min.)	0.097		0.174
Solvent (ml./min.)	12.78		12.89
Cocatalyst	(Ethyyl) <sub>1.5</sub> AlCl <sub>1.5</sub>		(Ethyyl) <sub>1.5</sub> AlCl <sub>1.5</sub>
Catalyst	VOCl <sub>3</sub>		VOCl <sub>3</sub>
Cocatalyst/catalyst ratio	5.0		5.9
Catalyst conc. in reactor millimoles/liter)	0.130		0.129
Reactor Temp., °C.	100		100
Reactor contact time (min.)	3.10		3.10
Ethylene conversion	0.650		0.620

TABLE VI (Continued)  
Effect of Al/V Ratio on Copolymer Homogeneity

Run No.	46	47
Copolymer Melt Index (M.I.)	1.50	1.13
Copolymer Stress Exponent	1.20	1.22
Copolymer Density	0.9281	0.9228
Copolymer Density (corr. to M.I. 1.0)	0.9270	0.9224
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	0.76	0.88
Copolymer side chain CH <sub>3</sub> /100C	0.70	0.80
Copolymer melting point, °C.	116.5	113.8
Homogeneity Index	100	106
Hydrogen (micromoles/min.)	7.0	5.9
Catalyst formation conditions	In situ	In situ

TABLE VII  
Effect of Vanadium Concentration on Copolymer Homogeneity

Run No.	48	49	50
Ethylene Feed (g./min.)	0.257	0.257	0.257
Comonomer	1-Butene	1-Butene	1-Butene
Comonomer Feed (g./min.)	0.0808	0.0473	0.105
Solvent (ml./min.)	12.88	12.69	13.98
Cocatalyst	(Ethyl)AlCl <sub>2</sub>	(Ethyl)AlCl <sub>2</sub>	(Ethyl)AlCl <sub>2</sub>
Catalyst	VOCl <sub>3</sub>	VOCl <sub>3</sub>	VOCl <sub>3</sub>
Cocatalyst/catalyst ratio	14.1	15.2	15.0
Catalyst conc. in reactor millimoles/liter)	0.538	0.261	0.127
Reactor Temp., °C.	100	100	100
Reactor contact time (min.)	3.09	3.13	3.11
Ethylene conversion	0.722	0.720	0.512

TABLE VII—Continued  
Effect of Vanadium Concentration on Copolymer Homogeneity

Run No.	48	49	50
Copolymer Melt Index (M.I.)	17.4	1.52	0.75
Copolymer Stress Exponent	—	—	—
Copolymer Density	0.9250	0.9277	0.9230
Copolymer Density (corr. to M.I. 1.0)	0.9195	0.9267	0.9239
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.46	0.96	1.20
Copolymer side chain CH <sub>3</sub> /100C	1.33	0.87	1.15
Copolymer melting point, °C.	109.9	114.4	109.6
Homogeneity Index	66	86	97
Hydrogen (micromoles/min.)	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ

TABLE VII (Continued)  
Effect of Vanadium Concentration on Copolymer Homogeneity

Run No.	51	52	53	54
Ethylene Feed (g./min.)	0.257	0.257	0.257	0.257
Comonomer	1-Octene	1-Octene	1-Octene	1-Octene
Comonomer Feed (g./min.)	0.257	0.257	0.257	0.259
Solvent (ml./min.)	12.62	12.22	12.16	13.48
Cocatalyst	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>	(Ethy)AlCl <sub>2</sub>
Catalyst	VOCl <sub>3</sub>	VOCl <sub>3</sub>	VO(O-n-butyl) <sub>2</sub> Cl	VO(O-n-butyl) <sub>2</sub> Cl
Cocatalyst/catalyst ratio	15.0	15.3	14.4	15.4
Catalyst conc. in reactor millimoles/liter)	0.528	0.132	0.546	0.252
Reactor Temp., °C.	105	100	100	100
Reactor contact time (min.)	3.16	3.25	3.26	2.94
Ethylene conversion	0.605	0.445	0.650	0.572

TABLE VII (Continued)  
Effect of Vanadium Concentration on Copolymer Homogeneity

Run No.	51	52	53	54
Copolymer Melt Index (M.I.)	1.28	5.21	20.4	22.5
Copolymer Stress Exponent	2.05	1.19	—	—
Copolymer Density	0.9287	0.9259	0.9237	0.9259
Copolymer Density (corr. to M.I. 1.0)	0.9280	0.9223	0.9179	0.9200
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	1.40	1.02	1.49	1.21
Copolymer side chain CH <sub>3</sub> /100C	1.26	0.91	1.33	1.08
Copolymer melting point, °C.	107.2, 115.1, 118.8	112.6	109.6	109.2
Homogeneity Index	10	95	66	97
Hydrogen (micromoles/min.)	nil	nil	nil	nil
Catalyst formation conditions	In situ	In situ	In situ	In situ

TABLE VIII  
Homogeneous Terpolymers

Run No.		55		56
Ethylene Feed (g./min.)		0.257		0.257
Comonomer	1-Butene	1-Octene	1-Octene	Propylene
Comonomer Feed (g./min.)	0.0658	0.0974	0.0974	0.0488
Solvent (ml./min.)		13.29		13.67
Cocatalyst	(Ethyl) AlCl <sub>3</sub>	(Ethyl) AlCl <sub>2</sub>		
Catalyst	VO(O-n-buty) <sub>3</sub>	VO(O-n-buty) <sub>3</sub>		
Cocatalyst/catalyst ratio	14.7	14.7	15.0	
Catalyst conc. in reactor millimoles/liter)		0.127		0.119
Reactor Temp., °C.		100	100	
Reactor contact time (min.)		3.00		2.91
Ethylene conversion		0.603		0.680
Copolymer Melt Index (M.I.)		1.27		3.10

TABLE VIII—Continued  
Homogeneous Terpolymers

Run No.	55	56
Copolymer Stress Exponent	1.16	1.15
Copolymer Density	0.9223	0.9173
Copolymer Density (corr. to M.I. 1.0)	0.9217	0.9147
Copolymer total CH <sub>3</sub> /100C and vinyl unsaturation	0.94	
Copolymer side chain CH <sub>3</sub> /100C	0.43 0.50	hexyl* ethyl
Copolymer melting point, °C.	111.3	105.8
Homogeneity Index	120	— **
Hydrogen (micromoles/min.)	nil	nil
Catalyst formation conditions	In situ	In situ

\* Estimated from comonomer reactivity data.

\*\* Copolymers containing methyl side chains do not fit the correlation of Figure I.

Runs 1 and 2 in Table I illustrate the copolymerization of ethylene with 1-butene and 1-octene respectively using coordination catalysts and reaction conditions of the prior art. The heterogeneous ethylene/1-butene copolymer of Run 1 shows a relationship between crystalline melting point and comonomer content which falls on line A of Figure I and between copolymer density and comonomer content which falls on line A of Figure II. The heterogeneous ethylene/1-octene copolymer of Run 2 shows a similar relationship between crystalline melting point and comonomer content and between copolymer density and comonomer content.

Runs 3 to 10 of Table I illustrate the copolymerization of ethylene with 1-butene (runs 3, 4, 5, 6 and 9) and with 1-octene (runs 7, 8 and 10) using synthesis conditions and catalyst formulations recommended by the prior art for the preparation of ethylene-propylene copolymers. The copolymers produced in Runs 3 to 10 are similar to heterogeneous copolymers of Runs 1 and 2 as shown by comparison of the crystalline melting point and/or density of these copolymers (as a function of their comonomer content). It is apparent that the coordination catalyst systems of Runs 3 to 10 offer little or no improvement over the standard coordination catalysts of Runs 1 and 2.

Runs 11 to 28 illustrate the copolymerization of ethylene with 1-butene, 1-octene and 1-octadecene using reaction conditions equivalent to those used in Runs 3 to 10 except for the reactor temperature and the composition and concentration of the catalyst systems used. The copolymers produced show crystalline melting points which are sharp and well defined. Regression analysis of these data gave the relationship between melting point and comonomer content as shown in equation 2 and plotted as line B in Figure I. The lower crystalline melting point of these copolymers in comparison with the heterogeneous copolymers of line A of Figure I indicates the difference in structure between the two types of copolymers. Furthermore, it indicates that the lower melting copolymers contain less of the longer ethylene sequences (at a given comonomer content) than the higher melting counterparts and have a more homogeneous overall comonomer distribution.

Typical catalysts for copolymerization of ethylene and propylene to rubber-like copolymers based on alkyl aluminum halides and vanadium derivatives fail to produce partly crystalline homogeneous  $\alpha$ -olefin copolymers under solution process conditions due to a combination of process and catalyst variables.

A comparison of the results of Runs 29 and 30 indicates that the ease of homogeneous copolymerization is an inverse function of the comonomer size. These runs illustrate the copolymerization of ethylene with 1-octene (Run 29) and with 1-octadecene (Run 30) under similar reaction conditions using ethylaluminum dichloride and vanadium oxychloride as the catalyst components. The data of Runs 31 to 34, Table III indicate a similar decrease in copolymer homogeneity index when using 1-butene comonomer in place of 1-octene comonomer with the same catalyst system. In general, it is observed that the catalysts which are suitable for the copolymerization of higher  $\alpha$ -olefins are more limited than those suitable for copolymerization of the lower  $\alpha$ -olefins.

Runs 33 and 34 illustrate the effect of increasing the reactor temperature in the copolymerization of ethylene with 1-butene using an  $(\text{ethyl})_2\text{AlCl}_2\text{-VO}(\text{O-n-butyl})_3$  catalyst system. At reactor temperatures above 130°C., the butene copolymer crystalline melting point increases at a given comonomer content indicating an increase in copolymer heterogeneity. Runs 37 to 39 illustrate the effect of temperature on octene copolymer homogeneity using the catalyst system  $(\text{ethyl})_{1.5}\text{AlCl}_{1.5}\text{-VOCl}_3$  and runs 35 and 36 show the same effect with the  $(\text{ethyl})_{1.5}\text{AlCl}_{1.5}\text{-VO}(\text{O-n-decyl})_2\text{Cl}$  catalyst system. These data show that the maximum reactor temperature for the synthesis of octene copolymers of homogeneity index >75 is in the range 110 to 115°C., although the temperature may be slightly higher for the synthesis of butene copolymers.

Runs 40 to 41, Table V, illustrate the low copolymer homogeneity obtained when  $\text{R}_2\text{AlCl}$  is used as alkylating agent rather than  $\text{R}_{1.5}\text{-AlCl}_{1.5}$  (Run 13, Table III) or  $\text{RAICl}_2$  (Run 14, Table II). This pronounced change in copolymer homogeneity between an alkyl/aluminum ratio of 1.5 and an alkyl/aluminum ratio of 2 was totally unexpected based on the prior art.

Runs 42 to 45 Table VI illustrate the effect of the ratio of the alkyl aluminum halide to the vanadium compound  $\text{VO}(\text{O-n-butyl})_3$  on butene copolymer homogeneity (Run 42) and on octene copolymer homogeneity (Runs 43 to 45). For  $\text{VO}(\text{OR})_n\text{X}_{3-n}$  based catalyst systems where  $n \geq 1$ , the minimum Al/V ratio is dependent on the particular comonomer used. Long chain  $\alpha$ -olefins such as 1-octene, require a higher Al/V ratio than shorter chain  $\alpha$ -olefins, such as 1-butene. The data indicate that a minimum Al/V ratio of about 5/1 for butene copolymers must be maintained in the reactor and that the minimum Al/V ratio for octene copolymers is about 9/1. For  $\alpha$ -olefins of  $\text{C}_{10}$  to  $\text{C}_{20}$ , an Al/V ratio of at least 12/1 should be maintained in the reactor.

With  $\text{VOCl}_3$  based catalyst systems, on the other hand, an Al/V ratio of  $\geq 5$  is suitable for homogeneous copolymerization of either butene (Run 46, Table VI) or octene (Run 47, Table VI) but 1-octadecene cannot be homogeneously copolymerized with this catalyst

\*Equimolar mixture of  $(\text{ethyl})_2\text{AlCl}$  and  $(\text{ethyl})\text{-AlCl}_2$ .

system even at high Al/V ratios (Run 30, Table III).

Runs 48 to 54, Table VII, illustrate the effect of vanadium concentration in the reactor on copolymer homogeneity. The results indicate that in order to obtain homogeneous octene copolymer, the vanadium concentration should not exceed about 0.16 mmole/litre for systems based on  $\text{VOCl}_3$  (Runs 51 and 52) and about 0.260 mole/litre for systems based on  $\text{VO}(\text{OR})_2\text{Cl}$  (Runs 53 and 54). The catalyst concentration effect is less pronounced with shorter chain  $\alpha$ -olefins, such as 1-butene, but Runs 48 to 50 indicate that with  $\text{VOCl}_3$ , the highest level of homogeneity is obtained at catalyst concentrations below about 0.260 mmole/litre.

The effect of the chemical structure of the vanadium compound on copolymer homogeneity is intimately related to  $\alpha$ -olefin comonomer size, vanadium concentration in the reactor, reactor temperature, Al/V ratio and R/Al ratio in the alkyl aluminum halide. When the other variables affecting comonomer distribution are not adjusted to optimum values trialkyl vanadates and dialkyl chlorovanadates show a reduced tendency to heterogeneous copolymerization in comparison with  $\text{VOCl}_3$  or  $\text{VCl}_4$ . A comparison of Runs 51 and 53, Table VII, shows that, at high vanadium concentrations using 1-octene as comonomer, di-n-butyl chlorovanadate (Run 53) produces a significantly more homogeneous copolymer than does

$\text{VOCl}_3$  (Run 51). Even under optimum conditions,  $\text{VOCl}_3$  yields a heterogeneous copolymer with 1-octadecene (Run 30) while  $\text{VO}(\text{O}-n\text{-butyl})_3$  yields a homogeneous 1-octadecene copolymer under otherwise identical conditions (Run 19).

The present invention is also applicable to inter-polymers of ethylene and more than one  $\alpha$ -olefin when at least one of the  $\alpha$ -olefins contains four or more carbon atoms. Examples are the ethylene-octene-butene terpolymer of Run 55 and the ethylene-octene-propylene terpolymer of Run 56, Table VIII. These terpolymers are of practical interest because their physical properties are nearly equivalent to the corresponding octene copolymers and yet they contain considerably less of the high cost octene comonomer. The catalyst and cocatalyst in Runs 55 and 56 were  $\text{VO}(\text{O}-n\text{-butyl})_3$  and (ethyl) $\text{AlCl}_2$  respectively, however  $\text{VO}(\text{O}-n\text{-butyl})_2\text{Cl}$  or  $\text{VOCl}_3$  and (ethyl) $\text{AlCl}_{1.5}$  may be used instead.

It should be noted that the limits of any individual process variable defining the area in which homogeneous copolymers can be prepared pertain only when the other defining process variables are at or near their optimum value for homogeneous copolymerization.

The ethylene/1-butene copolymer produced in Run 1 using a prior art coordination catalyst was subjected to fractionation and the results tabulated in the following table.

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TABLE IX

## Copolymer Fractionation Data:

Copolymer No. Run  
Melt Index — 2.85  
Density — 0.9220

Amount Fractionated — 10.0 gms.  
% Recovery — 97.12

Fraction No.	Corr. Fraction Wt (gms.)	Cumulative Wt. %	FRACTIONATION				DSC Melting Point
			Inherent Viscosity	Wt. Average Molecular Wt. $M_w \times 10^{-3}$	Side Chain $CH_3/100 C$		
1	Used in refractionation —	—	—	—	—	—	—
2	0.576	51.85	1.78	74	1.58	—	—
3	0.797	44.98	1.22	46	1.73	—	—
4	1.293	34.53	0.84	29	1.99	—	—
5	0.530	25.42	0.65	19	2.15	—	—
6	0.717	19.18	0.48	13	2.31	—	—
7	0.148	14.86	0.34	8	—	—	—
8	1.402	7.06	0.29	6.6	—	—	—
REFRACTIONATION							
1	0.371	98.32	5.22	320	0.77	—	—
2	0.246	95.24	3.68	190	1.09	—	—
3	0.757	90.22	2.94	145	1.27	—	—
4	0.578	83.55	2.29	105	1.21	—	—
5	0.334	78.99	1.93	84	1.48	—	—
6	0.581	74.41	1.62	66	1.60	—	—
7	0.410	69.46	1.37	52	1.72	—	—
8	0.479	65.01	1.18	44	1.91	—	—
9	0.204	61.60	1.14	39	—	—	—
10	0.171	59.72	0.92	31	—	—	—
11	0.414	56.80	0.77	25	—	—	—
WHOLE POLYMER							
			1.37	77	1.80	116.7	—

From the above table, it is evident that the copolymer is heterogeneous in composition, that is, the comonomer content is not constant over the various molecular weight fractions.

5 It should also be noted with respect to the comonomer distribution of these heterogeneous copolymers that the molecular weight fractions have crystalline melting points falling on line B of Figure I. This indicates that the fractions  
10 are sharp in molecular weight but not in co-

monomer distribution and the overall comonomer distribution of the whole copolymer must be considerably broader than the copolymer analysis of the fractions would indicate.

The ethylene/1-butene copolymer produced in Run 3 using a coordination catalyst system recommended for ethylene/propylene rubbers, was subjected to fractionation and the results are tabulated in the following table.

15

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TABLE X  
 Copolymer Fractionation Data:  
 Copolymer No. Run 3, Table I  
 Melt Index — 2.21  
 Density — 0.9206  
 Amount Fractionated — 10.0 gms.  
 % Recovery 95.01

Fraction No.	Corr. Fraction Wt. (gms.)	Cumulative Wt. %	Inherent Viscosity	FRACTIONATION		
				Wt. Average Molecular Wt. $M_w \times 10^{-3}$	Side Chain $CH_3/100 C$	DSC Melting Point
1	Used in refractionation —	—	—	—	—	—
2	0.598	55.42	1.49	59	2.09	—
3	0.744	48.91	0.93	31.5	2.47	—
4	0.475	42.81	0.77	24.5	2.67	—
5	1.296	33.96	0.58	17	2.43	—
6	0.222	26.37	0.46	12	2.48	—
7	0.881	20.85	0.37	9	2.52	—
8	1.645	8.24	0.17	3.2	—	—
REFRACTIONATION						
1	0.331	98.28	6.25	410	0.64	—
2	0.331	94.97	4.67	275	0.91	—
3	0.346	91.59	3.55	190	—	—
4	0.563	87.04	2.94	150	0.90	—
5	0.487	81.79	2.33	108	0.95	—
6	0.559	76.56	1.94	84	1.07	—
7	0.406	71.74	1.62	66	—	—
8	0.481	67.30	1.33	51	—	—
9	0.252	63.64	1.07	37	1.22	—
10	0.139	61.68	0.77	24.5	—	—
11	0.278	59.60	0.62	18	—	—
Whole Polymer			1.32	73	1.70	—

**10** The copolymer is heterogeneous and shows no improvement over the ethylene/11-benene copolymers prepared in Run 1. Similarly, the ethylene/11-octene copolymer produced in Run 8 using catalyst formulations recommended for ethylene/propylene rubbers was subjected to fractionation and found to be heterogeneous, as shown by the following table.

**5**  
Density — 0.9347  
Amount Fractionated — 10.0 g.  
% Recovery 96.8

TABLE XI

## Copolymer Fractionation Data:

Fraction No.	Corr. Wt. (gms.)	Fraction	Cumulative Wt. %	Inherent Viscosity	$M_w \times 10^{-3}$	Side Chain $CH_3/100 C$	DSC Melting Point	FRACTIONATION	
								—	—
1	Used in refractionation	—	—	—	—	—	—	—	—
2	0.108	63.73	1.21	45	—	—	—	—	—
3	0.651	59.93	0.71	21.8	1.12	—	—	—	—
4	2.057	46.39	0.64	19	1.23	—	—	—	—
5	0.374	34.24	0.53	14.5	1.23	—	—	—	—
6	0.909	27.82	0.45	11.5	1.20	—	—	—	—
7	0.698	19.79	0.34	8	1.26	—	—	—	—
8	1.630	8.23	0.26	5.6	—	—	—	—	—
REFRACTIONATION									
1	0.618	96.84	8.48	620	—	—	—	—	—
2	0.362	91.94	6.75	428	0.35	—	—	—	—
3	0.380	88.23	4.70	280	0.60	—	—	—	—
4	0.237	85.14	3.81	212	0.73	—	—	—	—
5	0.216	82.88	2.98	150	0.78	—	—	—	—
6	0.327	80.16	2.70	132	0.68	—	—	—	—
7	0.272	77.17	2.14	96	0.77	—	—	—	—
8	0.191	74.85	1.51	60	0.87	—	—	—	—
9	0.278	72.51	1.12	40	0.93	—	—	—	—
10	0.258	69.83	0.86	28	0.98	—	—	—	—
11	0.427	66.40	0.58	16.5	—	—	—	—	—
Whole Polymer			1.73	107	0.98	105.9, 109.5, 117.5	—	—	—

The ethylene/1-butene copolymer of Run 28, prepared in accordance with the present invention using a catalyst prepared by mixing ethyl aluminum dichloride and vanadium oxychloride, was subjected to fractionation. The results are tabulated in the following table.

TABLE XII

## Copolymer Fractionation Data:

Copolymer No. Run 28, Table II			Amount Fractionated — 10.0 gms. % Recovery — 96.80		
Fraction No.	Corr. Fraction Wt. (gms.)	Cumulative Wt. %	Inherent Viscosity	Wt. Average Molecular Wt. $M_w \times 10^{-3}$	Side Chain $\text{CH}_3/100 \text{ C}$
1	Used in refractionation	—	—	—	—
2	0.566	31.17	1.01	35.5	1.33
3	0.929	23.69	0.84	27	1.48
4	0.314	17.48	0.64	19	1.49
5	0.295	14.43	0.54	15	1.44
6	0.270	11.61	0.44	11.4	1.42
7	0.331	8.60	0.38	9.2	1.46
8	0.695	3.67	0.31	6	—

## FRACTIONATION

Fraction No.	Corr. Fraction Wt. (gms.)	Cumulative Wt. %	Inherent Viscosity	Wt. Average Molecular Wt. $M_w \times 10^{-3}$	Side Chain $\text{CH}_3/100 \text{ C}$	DSC Melting Point
1	0.711	96.45	1.93	84	1.35	—
2	0.361	91.09	1.43	56	1.29	—
3	0.846	85.06	1.30	50	1.44	—
4	0.847	76.59	1.24	46	1.47	—
5	0.629	69.21	1.11	40	1.42	—
6	0.615	62.99	1.03	36	1.32	—
7	0.571	57.06	0.95	32.5	1.32	—
8	0.623	51.09	0.84	27	1.46	—
9	0.532	45.32	0.77	24	1.44	—
10	0.374	40.79	0.68	20.5	1.42	—
11	0.492	36.46	0.57	16	1.40	—
Whole Polymer			0.95	47	1.40	103.9

## REFRACTIONATION

The results show that all the molecular weight fractions contain equivalent amounts of comonomer.

A homogeneous, random ethylene/1-butene copolymer prepared according to the process of the present invention was extruded in blown film form. The properties of this film were then compared with the properties of film prepared from conventional ethylene/1-butene copolymer. The results of the comparisons are tabulated in the following tables. 10

TABLE XIII  
Physical Properties of Blown Copolymer Film\*

Copolymer Type	Homogeneous-Random Butene Copolymer	Heterogeneous-Random Butene Copolymer
Copolymer melt index	1.94	1.62
Copolymer stress exponent	1.22	1.31
Copolymer density	0.9189	0.9190
 Film properties		
Elastic modulus MD (p.s.i.)	24600	24500
TD	25600	29600
Haze	13.9	31.1
Gloss outside	45	8
inside	47	10
 Tensiles MD		
Elongation %	725	825
Yield Str. psi.	1600	1650
Ult. Br. Str. psi.	4400	4400
 Tensiles TD		
Elongation %	750	900
Yield Str. psi.	1600	1600
Ult. Br. Str. psi.	4350	4100
Gauge mils	2.46	2.45
Impact strength 26" Dart test gms/mil	139	109

\* Extruder type 2" Royle, die gap 25 mil.

TABLE XIV  
Tear Strengths of Extruded Flat Film\*

Copolymer	Extrusion Draw Ratio	Film Thickness (mils)	Elmendorf Tear Strength (gms/mil)		TD/MD Tear Ratio
			TD	MD	
Homogeneous-random octene copolymer: Melt Index — 2.2 Density — 0.9195	14.5 18.9 29.8	1.17 0.90 0.57	370 380 459	290 238 202	1.3 1.6 2.3
Heterogeneous-random octene copolymer: Melt Index — 1.8 Density — 0.9185	9.2 13.4 17.0 28.4	1.85 1.27 1.00 0.60	350 443 577 658	197 156 124 72	1.8 2.8 4.6 9.1

\* Film extruded on small Instrom (Trade Mark) mounted ram extruder.

The copolymers of the present invention are of practical importance because of the effect of the homogeneous comonomer distribution and narrow molecular weight distribution on their physical and optical properties. Films of these copolymers show a reduced haze level, higher impact strength, reduced tendency towards delamination, and a better balance of physical properties in the machine and transverse directions.

WHAT WE CLAIM IS:—

1. A continuous process for the preparation of a homogeneous random partly crystalline copolymer (as herein defined) of narrow molecular weight distribution comprising ethylene and at least one other  $\alpha$ -olefin, at least one such other  $\alpha$ -olefin having four or more carbon atoms, which process comprises polymerizing the monomers dissolved in an inert nonpolymerizable solvent therefor and for the copolymer to be prepared in an agitated reaction zone maintained at a pressure sufficient to maintain the monomers in solution and at a temperature of 40 to 110°C. in the presence of a catalyst prepared by mixing (A) an organoaluminum halide  $R_nAlX_{3-n}$  wherein R is an alkyl or aryl radical, n is not greater than 1.5 or less than 1.0 and X is Cl or Br and (B) a vanadium compound selected from (1)  $VO(OOR)_mX_{3-m}$  where R is an alkyl or aryl radical, m is not less than 1 or more than 3, and X is Cl or Br and (2) vanadium oxyhalides soluble in the reaction medium; provided that when the vanadium compound is of type (1), the vanadium concentration in the reaction zone is not greater than 0.260 millimoles/liter of solution and the Al/V ratio in the reaction zone is not less than 5/1 when the  $\alpha$ -olefin is a  $C_4$  to  $C_6$   $\alpha$ -olefin, not less than 9/1 when the  $\alpha$ -olefin is a  $C_6$  to  $C_9$   $\alpha$ -olefin and not less than 12/1 when the  $\alpha$ -olefin is a  $C_{10}$  to  $C_{20}$   $\alpha$ -olefin and that when the vanadium compound is of type (2) the vanadium concentration in the reactor is not greater than 0.160 millimoles/liter of solution and the Al/V ratio in the reaction zone is not less than 5/1 when the  $\alpha$ -olefin is a  $C_4$  to  $C_6$   $\alpha$ -olefin.
2. A process according to claim 1, in which the  $\alpha$ -olefin is 1-butene, 1-octene, a mixture of 1-butene and 1-octene, or a mixture of 1-octene and propylene.
3. A process according to claim 2, in which the catalyst component (A) is  $(ethyl)_{1.5}AlCl_{1.5}$  and the catalyst component (B) is  $VO(O-n-butyl)_2Cl$ .
4. A process according to claim 2, in which the catalyst component (A) is  $(ethyl)_{1.5}AlCl_{1.5}$  and the catalyst component (B) is  $VOCl_5$ .
5. A process for the preparation of a homogeneous random partly crystalline copolymer according to claim 1 substantially as herein described in any of Runs 11 to 56.
6. A homogeneous random partly crystalline copolymer of ethylene and at least one other  $\alpha$ -olefin, at one such other  $\alpha$ -olefin having four or more carbon atoms, when prepared by the process claimed in any of claims 1 to 5.
7. A copolymer according to claim 6, not being formed from propylene, having a homogeneity index (as herein defined) in excess of 75.
8. A copolymer according to claim 7, having a homogeneity index in excess of 90.
9. A copolymer according to any of claims 6 to 8 in the form of a film.

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FIG. 1 COPOLYMER MELTING POINT VS. COMONOMER CONTENT

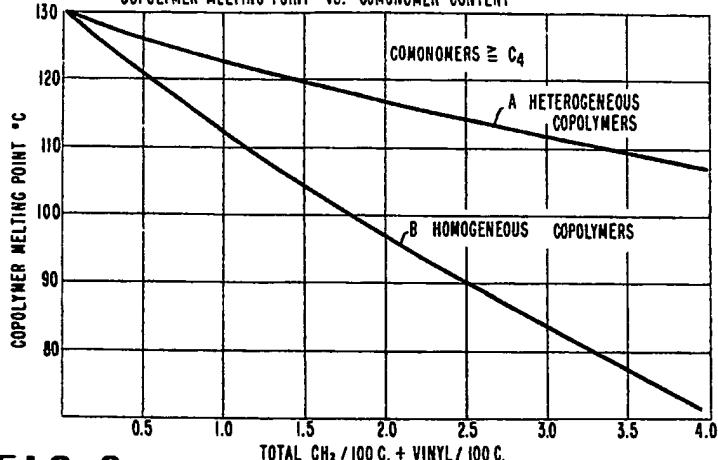
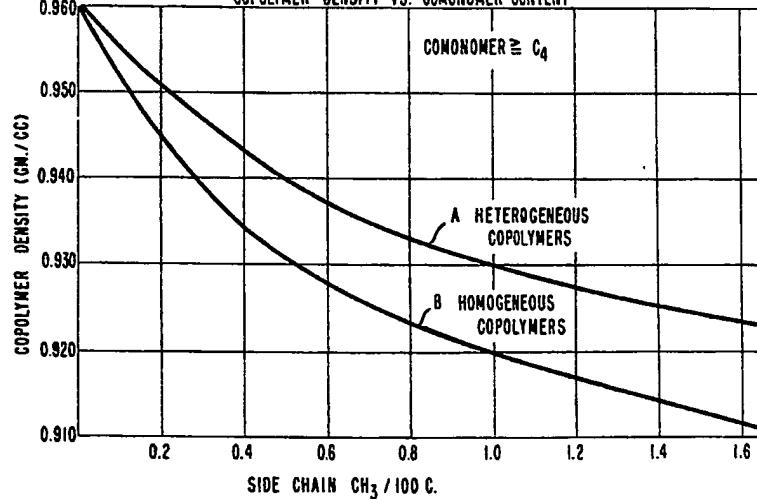


FIG. 2 COPOLYMER DENSITY VS. COMONOMER CONTENT



1209825

COMPLETE SPECIFICATION

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Sheet 2

FIG. 3

DENSITY CORRECTION FOR MELT INDEX

